## What Is Claimed Is:

1. A mass calibration apparatus for a mass analyzer, comprising:

an ion source for providing analyte ions to the mass analyzer;

ion optics, situated between the ion source and the mass analyzer, for assisting the motion of the analyte ions from the ion source to the mass analyzer; and

a source of lock mass ions adjacent the ion optics for creating lock mass ions within the ion optics.

- 2. The mass calibration apparatus of claim 1, wherein the ion source is at substantially atmospheric pressure.
- 3. The mass calibration apparatus of claim 1, wherein the ion source is an electrospray ion source.
- 4. The mass calibration apparatus of claim 1, wherein a portion of the ion optics is at less than atmospheric pressure.
- 5. The mass calibration apparatus of claim 1, wherein the ion source is an APCI (Atmospheric Pressure Chemical Ionization) ion source.
- 6. The mass calibration apparatus of claim 1, wherein the ion source is an APPI (Atmospheric Pressure Photoionization) ion source.
- 7. The mass calibration apparatus of claim 1, wherein the ion source is a MALDI (Matrix-Assisted Laser Desorption Ionization) ion source.

- 8. The mass calibration apparatus of claim 1, wherein the ion source is an AP-MALDI (Atmospheric Pressure Matrix-Assisted Laser Desorption Ionization) ion source.
- 9. The mass calibration apparatus of claim 1, wherein the mass analyzer is a time-of-flight mass analyzer.
- 10. The mass calibration apparatus of claim 1, wherein the ion optics comprises an ion guide.
- 11. The mass calibration apparatus of claim 1, wherein the ion optics system comprises an ion funnel.
- 12. The mass calibration apparatus of claim 1, wherein the ion optics system comprises a skimmer.
- 13. The mass calibration apparatus of claim 1, wherein the source of lock mass ions comprises a lock mass source adjacent the ion optics system for introducing lock mass molecules into the ion optics.
- 14. The mass calibration apparatus of claim 13, wherein the source of lock mass ions additionally comprises a lock mass ionization source adjacent the ion optics for ionizing lock mass molecules within the ion optics.
- 15. The mass calibration apparatus of claim 13, wherein the lock mass source comprises a gas source.

- 16. The mass calibration apparatus of claim 1, wherein the source of lock mass ions comprises a lock mass ionization source adjacent the ion optics for ionizing lock mass molecules within the ion optics.
- 17. The mass calibration apparatus of claim 16, wherein the lock mass ionization source comprises a laser.
- 18. The mass calibration apparatus of claim 16, wherein the lock mass ionization source comprises a source of ultraviolet radiation.
- 19. The mass calibration apparatus of claim 18, wherein the source of ultraviolet radiation comprises an ultraviolet lamp.
- 20. The mass calibration apparatus of claim 16, further comprising:

an ion optics path, within the ion optics, along which analyte ions traverse in passing from the ion source to the mass analyzer; and

the lock mass ionization source comprises an ultraviolet lamp surrounding a portion of the ion optics path for ionizing lock mass molecules in said portion of the ion optics path.

21. A mass calibration apparatus for a tandem mass spectrometer comprising:

a collision cell for fragmenting analyte ions; and

a source of lock mass ions adjacent said collision cell for creating lock mass ions in the collision cell.

22. The mass calibration apparatus of claim 21, wherein the source of lock mass ions comprises a lock mass source adjacent the collision cell for introducing lock mass molecules into the collision cell.

- 23. The mass calibration apparatus of claim 22, wherein the source of lock mass ions additionally comprises a lock mass ionization source adjacent the collision cell for ionizing lock mass molecules within the collision cell.
- 24. The mass calibration apparatus of claim 22 wherein the lock mass source comprises a gas source.
- 25. The mass calibration apparatus of claim 21 wherein the source of lock mass ions comprises a lock mass ionization source adjacent the collision cell for ionizing lock mass molecules within the collision cell.
- 26. A mass calibration apparatus for a tandem mass spectrometer comprising:

ion optics for transporting analyte daughter ions; and
a source of lock mass ions adjacent said ion optics for creating lock
mass ions in the ion optics.

- 27. The mass calibration apparatus of claim 26, wherein the source of lock mass ions comprises a lock mass source adjacent the ion optics for introducing lock mass molecules into the ion optics.
- 28. The mass calibration apparatus of claim 27, wherein the source of lock mass ions additionally comprises a lock mass ionization source adjacent the ion optics for ionizing lock mass molecules within the ion optics.
- 29. The mass calibration apparatus of claim 27, wherein the lock mass source comprises a gas source

- 30. The mass calibration apparatus of claim 26, wherein the source of lock mass ions comprises a lock mass ionization source adjacent the ion optics for ionizing lock mass molecules within the ion optics.
- 31. A mass spectrometer system comprising the mass calibration apparatus of claim 1.
- 32. A tandem mass spectrometer system comprising the mass calibration apparatus of claim 21.
- 33. A tandem mass spectrometer system comprising the mass calibration apparatus of claim 26.
- 34. A method for mass calibration of analyte ions with lock masses in a mass spectrometer that includes an analyte ion source, ion optics, and a mass analyzer, said method comprising:

creating lock mass ions within the ion optics.

- 35. The method of claim 34, wherein the step of creating lock mass ions comprises introducing lock mass molecules into the ion optics.
- 36. The method of claim 34, wherein the step of creating lock mass ions comprises ionizing lock mass molecules within the ion optics.
- 37. A method for mass calibration of analyte ions with lock masses in a mass spectrometer that includes an analyte ion source, ion optics and a mass analyzer, said method comprising:

introducing lock mass molecules into the ion optics; and ionizing the lock mass molecules within the ion optics.

- 38. The method of claim 37, wherein the step of ionizing the lock mass molecules comprises irradiating lock mass molecules with ultraviolet radiation.
- 39. A method for mass calibration of a tandem mass spectrometer that includes a collision cell, said method comprising:

creating lock mass ions within the collision cell.

- 40. The method of claim 39, wherein the step of creating lock mass ions comprises introducing lock mass molecules into the collision cell.
- 41. The method of claim 39, wherein the step of creating lock mass ions comprises ionizing lock mass molecules within the collision cell.
- 42. A method for mass calibration of a tandem mass spectrometer that includes a collision cell, said method comprising:

introducing lock mass molecules into the collision cell; and ionizing the lock mass molecules within the collision cell.

- 43. The method of claim 42, wherein the step of ionizing the lock mass molecules comprises irradiating lock mass molecules with ultraviolet radiation.
- 44. A method for mass calibration of a tandem mass spectrometer that includes ion optics for transporting analyte daughter ions to a mass analyzer, said method comprising:

creating lock mass ions within the ion optics.

- 45. The method of claim 44, wherein the step of creating lock mass ions comprises introducing lock mass molecules into the ion optics.
- 46. The method of claim 44, wherein the step of creating lock mass ions comprises ionizing lock mass molecules within the ion optics.
- 47. A method for mass calibration of a tandem mass spectrometer that includes ion optics for transporting analyte daughter ions to a mass analyzer, said method comprising:

introducing lock mass molecules into the ion optics; and ionizing the lock mass molecules within the ion optics.

48. The method of claim 47, wherein the step of ionizing the lock mass molecules comprises irradiating lock mass molecules with ultraviolet radiation.